MICRO-AND NANO-CRYSTALLINE DIAMOND FILM SYNTHESIS AT SUBSTRATE TEMPERATURES SUB 400°C

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Abstract

Two issues hamper the utilization of the outstanding properties of microcrystalline diamond (μ-D) in microelectronics: no electronic-grade n-type semiconducting diamond has been produced so far with good reproducibility, and most of the current growth processes are carried out at too high substrate temperature T_S, typically T_S>700°C. Electronic-grade n-type semiconducting diamond film deposition at lower substrate temperature is therefore of considerable interest.

We recently succeeded in making n-type diamond by sulfur doping[1]. The films were grown by hot-filament chemical vapor deposition (HFCVD) from $CH_4/H_2/H_2S$ gas mixture at T_S~700°C. With increasing sulfur content in the gas phase, the room temperature conductivity[2], the room temperature electron field emission properties[3], and the thermoionic emission at 340°C[4], were enhanced.

We were able to synthesize nanocrystalline diamond (n-D) at T_S~500°C by using the same technique and gas mixture[5]. The quality of n-D was shown to increase with the decrease of T_S (Figure 1). When 2.0% CH_4 was employed without H_2S, only nanocomposite carbon was grown, but the addition of 500 ppm H_2S and the reduction of T_S resulted in mixed μ-D and n-D (Figure 1). In addition, it was reported that the addition of sulfur in the gas phase induces a significant increase in the growth rate. At T_S~700°C it was possible to obtain a four-fold increase in the μ-D deposition rate, from 0.1 to 0.4 μm/h. We were then able to produce high-quality μ-D and n-D at T_S~440°C (Figure 2)[6] on molybdenum and glass.

We now report on the growth of high-quality μ-D and n-D films by sulfur-assisted HFCVD at T_S<400°C, on temperature sensitive substrates of industrial interest, such as glass. We modified the CVD system in order to attain lower substrate temperatures. The effects on diamond growth and structure of sulfur addition, substrate temperature in the presence of sulfur, and substrate nature are investigated.

The possibility of growing diamond films at such low temperature is interpreted as resulting from profound changes in the gas phase chemistry when trace amounts of sulfur in the form of H_2S are added to the diamond chemical vapor deposition reaction, as observed by laser cavity ring-down absorption spectroscopy. In particular, H_2S leads to the formation of CS in the heat-activated volume around the filament, which turns back into H_2S in the cooler region above the substrate, enhancing the transport of carbon atoms to the growing film surface to form diamond. This enables the deposition of diamond at a lower temperature and at a higher rate.

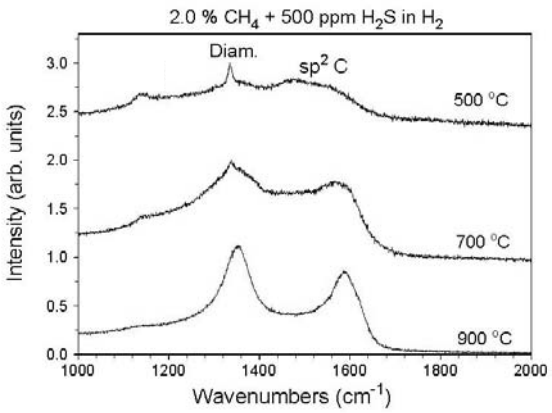

Figure 1. Visible Raman spectra of films grown with 2.0% CH_4 and 500 ppm H_2S as a function of substrate temperature. Diamond deposition is enabled at this high CH_4 concentration due to the presence of S and the lower substrate temperature.

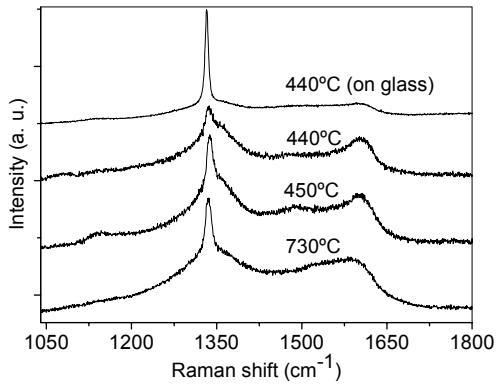

Figure 2. Visible Raman spectra showing the evolution of the diamond peak and sp^2-carbon related peaks as a function substrate temperature T_s. All substrates were Mo, except when indicated.

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